# B *K* and C *K* emission studies of superconductors: $YNi_2B_2C$ and LuNiBC

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## INTRODUCTION

Bulk superconductivity has been observed in Ni- and Pb-based rare-earth borocarbides [1, 2] with critical temperatures $T_c$ up to 23 K. This has raised questions about the understanding of the origin of superconductivity. One of which concerns the role of the transition metal nickel: if the Ni *3d* electrons are involved in the conductivity the electron-electron correlation (due to the presence of a partially filled *3d* band) may play a significant role in the determination of properties. Superconductivity has also been observed [2, 3] in the closely related RE-Ni-B-C system (RE = Y, Tm, Er, Ho, and Lu) with a maximum critical temperature of 16.6 K in non-magnetic $LuNi_2B_2C$ and 15.6 K for $YNi_2B_2C$.

The crystal structure for $LuNi_2B_2C$ and $YNi_2B_2C$ is a body centered tetragonal (bct) structure similar to the $ThCr_2Si_2$-type system with an additional carbon atom in lanthanide layer [4]. Local density approximation (LDA) band structure calculations [5, 6] have shown that, although Ni *3d* dominates near the Fermi Level ($E_F$), all four atoms are involved in the bands at $E_F$ and above. The states at Fermi level consist primarily of Ni *d*, B *p*, C *p*, and Lu *d*. The dispersion of the bands (with Lu *d* and Ni *d* + B *p* characters) along the *c* direction is comparable to that in the plane, giving a strongly three-dimensional (3D) character. Photoemission studies of $YNi_2B_2C$ [7, 8] show that Ni *3d* emission is expected at 1.5 eV below $E_F$, and that the structures at ~6, ~10, and ~14 eV have significant B and/or C *2sp* character.

Soft x-ray emission spectroscopy (SXES), probing the occupied part of the *2p* derived partial density of states (DOS), has been used in previous studies of the electronic structures of high temperature superconductors [9,10]. Here we report the SXES studies of the electronic structure of quaternary intermetallic compounds $YNi_2B_2C$ and LuNiBC and a comparison of the results to the calculated DOS of $LuNi_2B_2C$ and LuNiBC.

## EXPERIMENT

The samples were prepared by arc-melting and annealing. The starting materials are lanthanide (Y, Lu) shavings, pure Ni, B, and C powders. The phase purity of the samples was detected by x-ray powder diffraction. Both samples, $YNi_2B_2C$ and LuNiBC, were found to be phase pure within the resolution of the x-ray diffraction system. The $YNi_2B_2C$ and LuNiBC compunds are superconductors with $T_c \approx 16$ K and $T_c \approx 2.9$ K, respectively.

The experiments were performed at Beamline 7.0 of the Advanced Light Source (ALS) [11], Lawrence Berkeley Laboratory (LBL). This Beamline is comprised of a 5-meter, 5-cm-period undulator and a 10,000-resolving-power spherical grating monochromator (SGM) covering the spectral range from 100 to 1300 eV. The soft x-ray emission spectra was recorded using a high-resolution grazing-incidence grating spectrometer with two-dimensional detection [12].

In the SXES measurements the bandpass of the incoming photon beam was set to about 0.2 and 0.3 eV for boron and carbon, respectively. The spectrometer resolution was 0.25 eV and 0.45 eV for B and C *K*-emission measurements, respectively.

## RESULTS AND DISCUSSION

The B $K\alpha$ spectra of $YNi_2B_2C$ and LuNiBC with excitation energy above ionization threshold is shown in Figure 1. Although the B $K\alpha$ spectra of $YNi_2B_2C$ and LuNiBC show some differences on spectral profile in detail, both have a sharp edge at the high energy side. The B $K\alpha$ emission of $YNi_2B_2C$ exhibits a double-structure band with a 4.0 eV full width at half maximum (FWHM). The peak maximum and the high-energy shoulder are located at about 181.2 eV and 182.4 eV, respectively. The high-energy edge cut off at about 186.1 eV. In contrast, the B $K\alpha$ emission of LuNiBC exhibits a single-band dominant structure with a 2.7 eV FWHM, and peak maximum locates at about 182.0 eV. The high-energy edge cut off at about 186.0 eV.

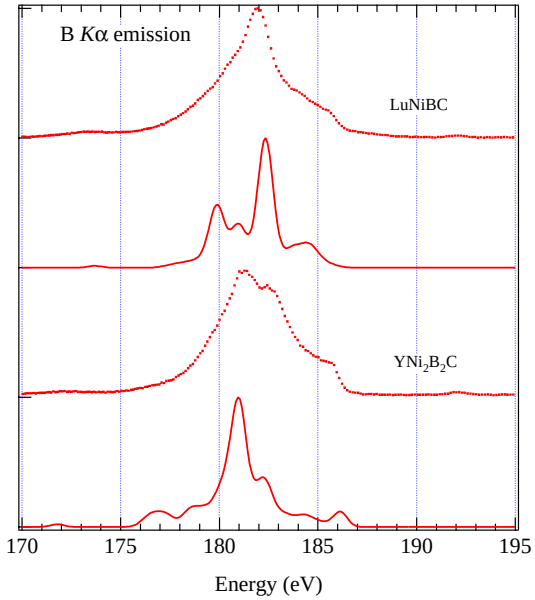


Figure 1: The B *K* x-ray emission of $YNi_2B_2C$ and LuNiBC with photon-excitation energy above the ionization threshold (open circles). The calculated B *p*-DOS of $LuNi_2B_2C$ and LuNiBC, obtained from an LDA band structure calculation [5], are displayed (solid curves). The calculated *p*-DOS was shifted so that the $E_F$ level is in accordance with the cut-off edge in the XES spectrum of $YNi_2B_2C$.

The calculated boron partial density of states of $LuNi_2B_2C$ and LuNiBC, obtained from LDA band structure calculation [5], are displayed in Figure 1. Because we are not aware of the calculated boron partial DOS of $YNi_2B_2C$ at present, the B $K\alpha$ emission spectrum of $YNi_2B_2C$ is compared with the boron partial DOS of $LuNi_2B_2C$ since the boron partial DOS of $YNi_2B_2C$ is very similar to that of $LuNi_2B_2C$. The energy scale of the calculated partial DOS was obtained by aligning the Fermi level, as indicated in the Figure 1, to the cut-off edge in the experimental spectrum of $YNi_2B_2C$. Both calculation results agree well with the B *K* emission spectra of $YNi_2B_2C$ and LuNiBC.

X-ray diffraction results showed that the crystal structure of $YNi_2B_2C$ and LuNiBC is a three-dimensionally connected framework [4], and it may be viewed as a layered system, reminiscent of the high-$T_c$ oxide superconductors. LuC, NaCl-type layers alternate with $Ni_2B_2$ layers, with a stoichiometry of 1:1 for $YNi_2B_2C$ (or 1:2 for LuNiBC). The $Ni_2B_2$ layers are two-dimensional networks of the inverse PbO-type, with nickel being tetrahedral-coordinated by four boron atoms. The $Ni_2B_2$ layers contain a square-planar $Ni_2$ array sandwiched between the boron planes. The tetrahedral-coordinated Ni produces Ni-B bonds that are relatively weak, and this leads to Ni-B hybridization effects that are moderate in strength.

B *2p* states mix with the Ni *4sp* band and form occupied bonding states *2p-4sp* with main *2p* character. The interaction between B *2p* and Ni *3d* electrons results in bonding and antibonding *2p-3d* states close to the Fermi level. The splitting between bonding and antibonding states is small since the interaction between the *2p* and *3d* states is weaker. In Ni the *3d* band in the formation of chemical bonds is positioned near the Fermi level, and there are empty states above the Fermi level. In this energy region, the B *2p* partial DOS is expected to be very low, as it was pointed out in the calculated B *2p* partial DOS of $LuNi_2B_2C$ [5, 6].

The predominant feature in the B $K\alpha$ emission spectrum of $YNi_2B_2C$, appearing at about 181.2 eV, has mainly pure B *2p* character. At higher emission energy in the B $K\alpha$ spectrum of $YNi_2B_2C$, a plateau of intensity appears which ends with a sharp edge at about 186.1 eV. The intensity at the Fermi level in B *K*-emission spectrum from $YNi_2B_2C$ is due to B *2p* - Ni *3d* hybridization with main *3d* character. The observed cut-off edge at the Fermi level in the XES spectrum indicates that the antibonding *2p-3d* states are partly occupied.

The C $K\alpha$ emission of $YNi_2B_2C$ and LuNiBC with photon-excitation energy above the ionization threshold are shown in Figure 2. The C $K\alpha$ emission of $YNi_2B_2C$ exhibits a double-band structure with a 6.1 eV FWHM. The peak maximum and the high-energy shoulder are located at about 276.6 eV and 279.59 eV, respectively. The C $K\alpha$ spectrum of LuNiBC also exhibits a double-band structure with a 5.4 eV FWHM and peak maximum located at about 278.4 and 280.5 eV, respectively.

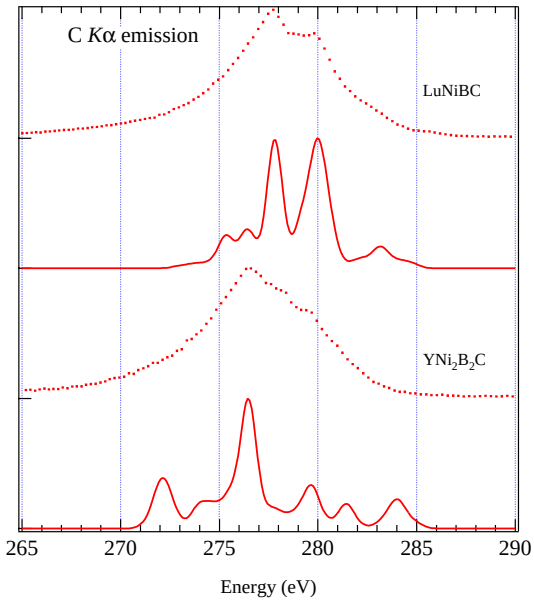


Figure 2: The C *K* x-ray emission of $YNi_2B_2C$ and LuNiBC with photon-excitation energy above the ionization threshold (open circles). The calculated C *p*-DOS of $LuNi_2B_2C$ and LuNiBC, obtained from an LDA band structure calculation [5], are displayed (solid curves). The calculated *p*-DOS was shifted to align the dominant features with respect to the same features in the XES spectrum of $YNi_2B_2C$.

The calculated carbon partial DOS of $LuNi_2B_2C$ and LuNiBC, obtained from the LDA band structure calculation [5], are displayed in Figure 2. The energy scale of calculated partial DOS was obtained by aligning the dominant features with respect to the same features in the experimental spectrum of $YNi_2B_2C$. The contributions from the lowest partial DOS bands, which have carbon *2s* character, are absent in the XES spectra due to their dipole forbidden nature. Both calculated carbon partial DOS are in very good agreements with the C $K\alpha$ spectra of $YNi_2B_2C$ and LuNiBC.

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